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Standard Recommended Practices for
GENERAL TECHNIQUES OF ULTRAVIOLET QUANTITATIVE ANALYSIS[1]

This Standard is issued under the fixed designation E 169; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval.

1. Scope

1.1 These recommended practices are intended to provide general information on the various techniques most often used in ultraviolet quantitative analysis. The purpose is to render unnecessary the repetition of these descriptions of techniques in individual methods for ultraviolet quantitative analysis.

2. Principle

2.1 Quantitative ultraviolet analysis is based upon the absorption law, known as Beer's law. The units of this law are defined in ASTM Definitions E 131, Terms and Symbols Relating to Molecular Spectroscopy.[2] Beer's law (Note), when applied to a mixture of n components, may be expressed in the following form (see Section 8):

$$A = a_1bc_1 + a_2bc_2 + \ldots + a_nbc_n$$

NOTE—Detailed discussion of the origin and validity of Beer's law may be found in the books and articles listed in the bibliography at the end of these recommended practices.

3. Sample Preparation

3.1 Weigh by difference the specified amount of the sample (solid or liquid) into the volumetric flask. Add the solvent and shake to dissolve the sample completely. Fill to the mark with solvent. (Solvent and flask should be at approximately the same temperature as the spectrophotometer.) If needed, a dilution should be made with a calibrated pipet and volumetric flask, using adequate volumes for accuracy. Fill the absorption cell with the solution and fill the comparison or blank cell with the pure solvent, which should match that used for the solution as closely as possible.

4. Base-Line and Cell Checking

4.1 The balance of the spectrophotometer should be checked at several wavelengths without cells in the beam for manually operated instruments; a baseline scan should be made with automatic recording instruments. Prior to analytical use, the cells should be checked against each other with pure solvent in each. A check for cell length matching may be made by examining a strongly absorbing solution versus a pure solvent, and then emptying, cleaning, and reloading solvent and sample into the other cells. Absorbance readings should check within 1 percent. The difference between the absorbance of the sample cell and the absorbance of the comparison or blank cell should be determined at each analytical wavelength with both cells filled with solvent. These differences, or cell corrections, should be added algebraically to the absorbance of the sample solution at the proper wavelength.

5. Analytical Wavelengths

5.1 Analytical wavelengths are those wavelengths at which absorbance readings are taken for use in calculations. These may include readings taken for purposes of background corrections. The analytical wavelengths are frequently chosen at absorption maxima; this is not necessarily always done. For example, use of isoabsorptive or isosbestic points is frequently helpful.

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[1] These recommended practices are under the jurisdiction of ASTM Committee E-13 on Molecular Spectroscopy.

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[2] *Annual Book of ASTM Standards*, Part 30.

By publication of this standard no position is taken with respect to the validity of any patent rights in connection therewith, and the American Society for Testing and Materials does not undertake to insure anyone utilizing the standard against liability for infringement of any Letters Patent nor assume any such liability.

5.2 On manually operated spectrophotometers, record the absorbance readings at the specified analytical wavelengths, operating the instrument in accordance with the recommendations of the manufacturer or ASTM Recommended Practice E 275, for Describing and Measuring Performance of Spectrophotometers.[2] On automatic recording spectrophotometers, record the absorbance readings from the chart at the analytical wavelengths. The wavelength region scanned should be somewhat greater than that required to contain only the analytical wavelengths. Take care to start the chart and scanning drives exactly together. End the scan well before the slit has opened fully.

5.3 Absorbance values should be used only if they fall within the acceptably accurate range of the particular spectrophotometer used. Generally, this means between absorbances of 0.1 and 1.0. (Refer to Recommended Practices E 275.) If the absorbance is too low, use either a longer absorption cell or prepare a new solution of higher concentration. If the absorbance is too high, use a shorter cell or make a quantitative dilution.

6. Slit Widths

6.1 If a fixed slit width is specified in the analytical method, this should be used, and the sensitivity control properly adjusted for balance. If no slit width is specified, the value of the slit width should be recorded. (Changes in the day-to-day values of slit width are often a clue to instrumental defects, dirt accumulation on optical parts, or deposition of films on the interior of the reference absorption cells.)

7. Solvents and Solvent Effects

7.1 The ultraviolet absorption spectrum of a compound will vary in different solvents depending on the chemical structures involved. Nonpolar solvents have the least effect on the absorption spectrum. Nonpolar molecules in most instances are not affected in polar solvents. However, polar molecules in polar solvents may show marked differences in their spectra. Any interaction between solute and solvents leads to a broadening and change in structural resolution of the absorption bands. Ionic forms may be created in acidic or basic solutions. In addition, there are possible chemical reactions between solute and solvent, and also photochemical reactions arising from either room illumination or the short wavelengths in the beam of the spectrophotometer. It is important that the solvent used be specified in recording spectral data. (The change in spectra between acidic and basic conditions may sometimes be employed in multicomponent analysis.)

7.2 Common, commercially available solvents of "spectroscopic purity" are listed in Table 1. The short wavelength limit is approximate, and refers to the wavelength at which a 1-cm light path length gives an absorbance of unity.

7.3 Water, and 0.1 *N* solutions of hydrochloric acid, sulfuric acid, and sodium hydroxide are commonly used as solvents. Buffered solutions, involving nonabsorbing materials, are frequently used; both the composition of the buffer and the measured pH should be specified. Mixtures of 0.1 *N* dihydrogen sodium phosphate and 0.1 *N* hydrogen disodium phosphate are useful in the 4.5 to 8.9 pH range. A table of nonabsorbing buffers has been presented by Abbott (**8**).[3]

8. Calculations

8.1 Quantitative analysis by ultraviolet spectrophotometry depends upon Beer's law. The terms and symbols used are those defined in Definitions E 131. According to Beer's law:

$$A = abc = (\epsilon/M) \times bc$$

where:

A = absorbance,
a = absorptivity,
b = cell length, cm,
c = concentration, g/liter,
ϵ = molar absorptivity, and
M = molecular weight.

8.1.1 In practice, a distinction must be made between c, the concentration of the absorbing material in the cell at the time of observation, and the concentration of the *absorbing material* in the *sample as received*. This is here designated as C and is in weight percent (g/100 g). The solution to be examined has a concentration of *sample* in solution, here designated as C_s, which is in units of grams per liter.

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[3] The boldface numbers refer to the bibliography at the end of these recommended practices.

$$c = A/ab$$

$$C\text{, percent} = (c/C_s) \times 100 = (A/abC_s) \times 100$$

8.2 If one or more dilutions have been made, the quantity called the dilution factor must be included. Dilution factor, f, is the ratio of the final volume to the initial volume. If more than one dilution is performed, the dilution factor is the product of the factors from each dilution. If dilutions are made, the equation becomes:

$$C\text{, percent} = (c/C_s) \times 100 = (Af/abC_s) \times 100$$

Note that c and C_s have the dimensions of grams per liter. If dilution is made, C_s is not the concentration in the cell at the time the absorbance is determined; the concentration in the cell is C_s/f.

8.3 *Standard Samples*—The absorptivity of the absorbing material, the concentration of which it is desired to determine, is obtained by examination of a pure sample of this material which is called a standard sample. However, if no such pure material is available, the best available sample is used, or a value of the absorptivity is taken from the literature. Take care to specify this, by reporting values as "percentage against standard sample" or by noting that the accuracy of the analysis is dependent upon a published value of the absorptivity or molar absorptivity. (A reference must be cited.)

8.4 *Types of Analyses* (see Fig. 1):

8.4.1 *One Component, No Background Correction:*

$$C\text{, percent} = (Af/abC_s) \times 100$$

8.4.2 *One Component, Simple Background Correction:*

$$C\text{, percent} = \frac{(A_1 - A_2) \times f}{a_1bC_s} \times 100$$

where the subscripts refer to analytical wavelengths. The term A_2 is the absorbance at the wavelength used for making a simple subtractive correction. It is usually selected from examination of the spectral curve of the standard, at a wavelength longer than that of A_1, preferably where a_2 is equal to or less than $a_1/100$.

8.4.3 *One Component with Slope-Type Background Correction:*

$$C\text{, percent} = \frac{(A_1 - SA_2) \times f}{a_1bC_s} \times 100$$

where:

S = slope between wavelengths 1 and 2 for the background, or the ratio of the background absorbance values at these wavelengths.

8.4.3.1 The background absorption is usually *not* linear between the analytical wavelength and the wavelength at which a simple subtractive background correction may be obtained. When it is possible to determine the slope between wavelengths 1 and 2 by observation of the samples that do not contain the absorbing material that is to be determined this may be used as a correction for the background absorption.

8.4.4 *One Component with Linear Background Correction:*

$$C\text{, percent} = \frac{A_1 - \dfrac{A_2 + A_3}{2}}{abC_s} \times 100$$

8.4.4.1 This method is especially effective with materials that have sharp bands. Wavelengths 2 and 3 are selected to the long and short wavelength sides of the analytical wavelength 1, usually at minima. The absorptivity a is here the "effective" absorptivity as determined on a pure sample, using the corrections, and is somewhat lower than the true or absolute absorptivity. The above expression holds only in the special case where the wavelength for A_1 is exactly midway between the wavelengths for A_2 and A_3. The equation for the general case is:

$$C\text{, percent} = \frac{f\left[A_1 - \left(A_3 + (A_2 - A_3) \times \dfrac{\lambda_3 - \lambda_1}{\lambda_3 - \lambda_2}\right)\right]}{abC_s} \times 100$$

8.4.5 *One Component with Background Correction from Outside Data:*

$$C\text{, percent} = \frac{(A - X) \times f}{abC_s} \times 100$$

8.4.5.1 This is a general case in which some empirical correction may be derived from data other than spectrophotometric, and is applied as an effective absorbance which is subtracted from the observed. As an example, the concentration of a known interfering material may be determined by titration, and the absorbance due to this calculated, and then subtracted.

8.4.6 *Two Components, with No Overlapping Absorption*—Apply method in 8.4.1

twice, at the two analytical wavelengths. This is an almost impossible case, except when the relative concentrations of the two components are such that the product of absorptivity and concentration of one component at a given wavelength is more than 100 times the product for the other component, allowing the latter to be neglected.

8.4.7 *Two Components, with Overlapping Absorption for Only One Component*—Determine the component with no interference (component x) at an analytical wavelength selected to allow no contribution from component y.

$$C_x\text{, percent} = (Af/a_1bC_s) \times 100$$

8.4.7.1 Calculate the contribution of this component to the observed absorbance at the other analytical wavelength, where both components are absorbing, as follows:

$$A_{2x} = a_{2x}bc_x$$

8.4.7.2 Calculate the concentration of component y as follows:

$$C_y\text{, percent} = [(A_2 - A_{2x}) \times f]/a_2bC_s$$

8.4.8 *Two Components, with Mutually Overlapping Absorption*—Use the absorbance-ratio method (graphical) described in the literature (**10**), or by simultaneous equations as follows:

$$C_x\text{, percent} = \frac{a_{y_2}A_1 - a_{y_1}A_2}{bC_s \times (a_{y_2}a_{x_1} - a_{y_1}a_{x_2})} \times 100$$

$$C_y\text{, percent} = \frac{a_{x_2}A_1 - a_{x_1}A_2}{bC_s \times (a_{y_1}a_{x_2} - a_{y_2}a_{x_1})} \times 100$$

8.4.9 *Inverted Matrix Method, for Two or More Components with Mutually Overlapping Absorption*—For information on the inverted matrix method, see Section 7.1 of ASTM Recommended Practices E168, for General Techniques of Infrared Quantitative Analysis[2] and the literature (**13**).

9. Presentation of Data

9.1 If absorption curves are to be presented with an analytical method, it is recommended that one of the following systems be used, with the wavelength (in nanometers) increasing linearly to the right:

log ϵ or log a plotted against λ

A plotted against λ

$\epsilon \times 10^{-n}$ or a plotted against λ

where the symbols are as defined in Definitions E 131. Marking the analytical wavelengths and absorptivity values on the curve is suggested for clarity, or a separate table of analytical wavelengths and absorptivities may be used. (These data are helpful for others who may wish to use the method in a somewhat modified form.)

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(**11**) Graff, M. M., O'Connor, R. T., and Skau, E. L., "Purification of Solvents for Absorption Spectroscopy," *Industrial and Engineering Chemistry*, Analytical Edition, IENAA, Vol 16, 1944, p. 556.

(**12**) Tunnicliff, D. D., "Solvents for Ultraviolet Spectrophotometry," *Talanta*, TLNTA, Vol 2, No. 4, 1959, p. 341.

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TABLE 1 Solvents[a]

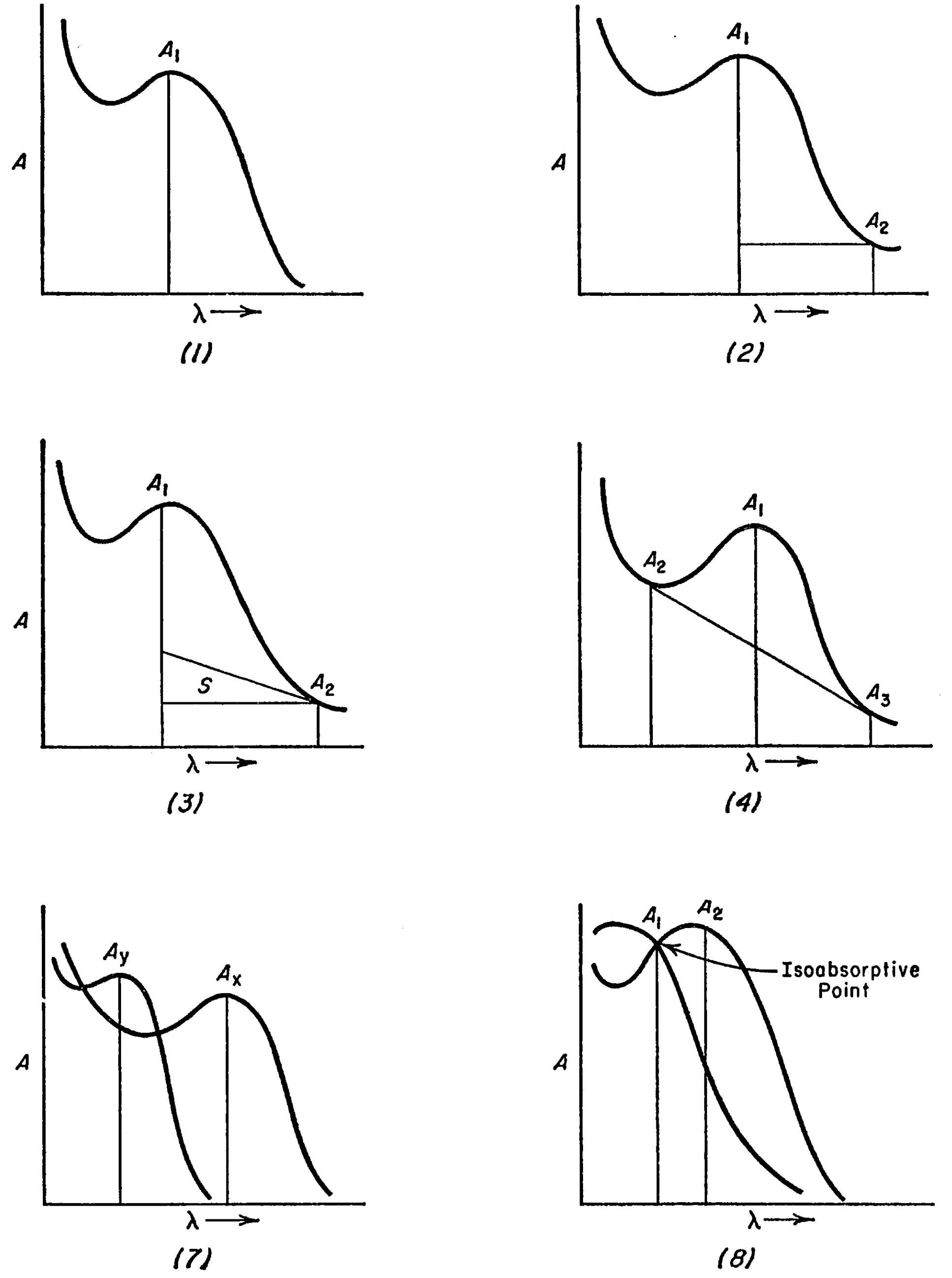
Solvent	Cutoff, nm
Pyridine	305
Tetrachloroethylene	290
Benzene	280
N,*N*-Dimethylformamide	270
Carbon tetrachloride	265
Methyl formate	260
Chloroform	245
Dichloromethane	235
Ethyl ether	220
Acetonitrile	215
Isopropyl alcohol	210
Ethyl alcohol	210
Methyl alcohol	210
Cyclohexane	<210
*Iso*octane	<210

[a] Procedures for special purification of solvents for further improvement in the wavelength limit are given in the literature (**11**, **12**). Solvents of high purity for use in absorption spectroscopy also are available commercially as follows:

Solvents for Spectrophotometric Use, Distillation Products Industries, Division of Eastman Kodak Co., Rochester, N. Y. 14603

Spectro Grade Solvents Fisher Scientific Co., 717 Forbes Ave., Pittsburgh, Pa. 15219

Spectroquality Solvents, Matheson, Coleman and Bell, 11-38 31st Ave., Long Island City, N. Y. 11106



(*1*) One Component, No Background Correction.
(*3*) One Component, with Slope-Type Background Correction.
(*7*) Two Components, with Overlapping Absorption for Only One Component.
(*2*) One Component, Simple Background Correction.
(*4*) One Component, with Linear Background Correction.
(*8*) Two Components, with Mutually Overlapping Absorption.

FIG. 1 Plot of Components.